Electronic Supplementary Material (ESI) for Photochemical & Photobiological Science

SUPPLEMENTARY INFORMATION

Photophysical Properties and Photochemistry of Substituted Cinnamates and Cinnamic Acids for UVB Blocking: Effect of Hydroxy, Nitro, and Fluoro Substitutions at *ortho*, *meta*, and *para* Positions

Malinee Promkatkaew,[1,2,4] Songwut Suramitr,[1,2] Thitinun Karpkird,[1]
Supason Wanichwecharungruang,[3] Masahiro Ehara,[4,5*] and Supa Hannongbua[1,2*]

[1]Department of Chemistry, Faculty of Science, Kasetsart University, Bangkok 10900, Thailand
[2]Center of Nanotechnology, Kasetsart University, Bangkok 10900, Thailand
[3]Department of Chemistry, Faculty of Science, Chulalongkorn Unverisity, Bangkok 10330, Thailand
[4]The Graduate University for Advanced Studies (SOKENDAI), 38 Nishigo-naka, Myodaiji, Okazaki 444-8585, Japan
[5]Institute for Molecular Science and Research Center for Computational Science, 38 Nishigo-naka, Myodaiji, Okazaki 444-8585, Japan

*Corresponding author e-mail: fscisph@ku.ac.th (S.H.); ehara@ims.ac.jp (M.E.)

SYNTHESIS AND CHARACTERIZATION

Materials: 2-Ethylhexanol and malonic acid were purchased from Fluka Chemical Company (Buchs, Switzerland). Piperidine was purchased from Sigma (Sigma Chemical Co., Steinheim, Germany). All benzaldyhydes, pyridine and 2-hydroxycinnamic acid (**1A**) were purchased from Acros (Geel, Belgium). Solvents used in syntheses and spectroscopic techniques were reagent or analytical grades purchased from Labscan (Bangkok, Thailand).

Instruments: UV–Vis absorption spectra were recorded in a quartz cell (light path, 10 mm) on a UV–Vis spectrophotometer (Perkin-Elmer, CT, USA). Fluorescence emission spectra were recorded in a fluorescence spectrophotometer (Cary Eclipse; Varian, CA, USA). All ^{1}H NMR spectra were obtained in $CDCl_3$ or DMSO-d_6 on a Varian Mercury NMR spectrometer, which operated at 400 MHz for ^{1}H and 100 MHz for ^{13}C nuclei.

Preparation of *Trans*-Substituted Cinnamic Acids: All *trans*-cinnamic acids were synthesized as described in the previous work using the methods of Koo *et al.* (1944) and Allen & Spangler (1943). In short, malonic acid (0.02 mol) and substituted benzaldehyde (0.015 mol) were dissolved in 5 ml of pyridine and piperidine (0.15 ml) was added. The reaction mixture was refluxed at 70°C for 5 hrs. After the mixture had been cooled, 5 ml of conc. HCl and 40 ml of cold water were added. The solid was separated by suction filtration, washed with cold water and recrystallized with ethanol.

3-hydroxycinnamic acid (**2A**): light brown solid (70% yield); ^{1}H-NMR (DMSO-d_6) δ(ppm): 7.50-7.46 (d, J = 16Hz, 1H), 7.21-7.17 (t, 1H), 7.08-7.06 (d, J = 8Hz, 1H), 7.00 (s, 1H), 6.83-6.81(d, J = 8Hz, 1H), 6.41-6.37 (d, J = 16Hz, 1H); ^{13}C-NMR (DMSO-d_6) δ(ppm): 167.5, 157.7, 144.1, 135.4, 130.1, 126.7, 119.4, 117.1, 114.5.

4-hydroxycinnamic acid (**3A**): white solid (72% yield); ^{1}H-NMR (DMSO-d_6) δ(ppm): 7.51-7.49 (d, J = 8 Hz, 2H), 7.50-7.46 (d, J = 16.00 Hz, 1H), 6.78-6.76 (d, J = 8Hz, 2H), 6.28-6.24 (d, J = 16 Hz, 1H); ^{13}C-NMR (DMSO-d_6) δ(ppm): 168.0, 159.7, 144.4, 130.9, 125.3, 115.9, 115.4.

2-nitrocinnamic acid (**4A**): white solid (79% yield); ^{1}H-NMR (DMSO-d_6) δ(ppm): 8.06-8.04 (d, J = 8 Hz, 1H), 7.92-7.90 (d, J = 8 Hz, 1H), 7.87-7.83 (d, J = 16 Hz, 1H), 7.78-7.74 (t, 1H), 7.67-

7.63 (t, 1H), 6.53-6.49 (d, J = 16 Hz, 1H); ^{13}C-NMR (DMSO-d_6) δ(ppm):166.8, 148.2, 138.8, 133.8, 130.7, 129.3, 124.6, 124.2, 123.4.

3-nitrocinnamic acid (**5A**): light brown solid (75% yield); ^{1}H-NMR (DMSO-d_6) δ(ppm): 8.49 (s, 1H), 8.23-8.20, 8.17-8.15 (dd, J = 8 Hz, 2H), 7.73-7.69 (d, J = 16 Hz, 1H), 7.71-7.69 (d, J = 8 Hz, 1H), 6.74-6.70 (d, J = 16 Hz, 1H); ^{13}C-NMR (DMSO-d_6) δ(ppm): 167.1, 148.2, 141.1, 136.0, 133.9, 130.2, 124.5, 123.9, 122.2.

4-nitrocinnamic acid (**6A**): white solid (60% yield); ^{1}H-NMR (DMSO-d_6) δ(ppm): 8.22-8.20 (d, J = 8 Hz, 2H), 7.94-7.92 (d, J = 8 Hz, 2H), 7.68-7.64 (d, J = 16 Hz, 1H), 6.72-6.68 (d, J = 16 Hz, 1H); ^{13}C-NMR (DMSO-d_6) δ(ppm): 167.0, 147.9, 145.9, 141.2, 129.1, 127.1, 123.6.

2-fluorocinnamic acid (**7A**): white solid (50% yield); ^{1}H-NMR (DMSO-d_6) δ(ppm): 7.79-7.75 (dd, 1H), 7.66-7.62 (d, J=16 Hz, 1H),7.46-7.41 (dd, 1H), 7.24-7.21 (m, 2H), 6.57- 6.53 (d, J=16 Hz, 1H); ^{13}C-NMR (DMSO-d_6) δ(ppm): 167.3, 161.7, 159.2, 135.6, 132.1, 129.2, 124.9, 121.3, 115.9.

3-fluorocinnamic acid (**8A**): white solid (76% yield); ^{1}H-NMR (DMSO-d_6) δ(ppm): 7.59-7.55 (d, J = 16.00 Hz,1H), 7.58 (s, 1H), 7.50-7.48 (d, J = 8Hz, 2H), 7.45-7.39 (dd, 1H), 7.23-7.19 (t, 1H), 6.61-6.57 (d, J = 16.00 Hz,1H); ^{13}C-NMR (DMSO-d_6) δ(ppm): 167.3, 163.6, 142.5, 136.8, 130.8, 124.6, 120.3, 116.9, 114.4.

4-fluorocinnamic acid (**9A**): white solid (80% yield); ^{1}H-NMR (DMSO-d_6) δ(ppm): 7.72-7.68 (dd, 2H), 7.58-7.54 (d, J=16 Hz, 1H), 7.20-7.16 (dd, 2H), 6.45-6.41 (d, J=16 Hz, 1H); ^{13}C-NMR (DMSO-d_6) δ(ppm): 167.5, 164.4, 161.9, 142.7, 130.5, 119.1, 116.0.

Preparation of 2-Ethylhexyl-*Trans*-Substituted Cinnamates: Syntheses were prepared according to the method of Womack & McWhirter. *Trans*-substituted cinnamic acid (0.01 mol) was dissolved in dichloromethane. Oxalylchloride (0.015 mol) was then added slowly under N_2. The reaction mixture was stirred at room temperature for 1.5 hrs. Residue oxalylchoride was removed by rotary evaporator before 2-ethylhexanol (0.01 mol) was added. The mixture was stirred overnight at room temperature. The residue obtained after solvent evaporation was washed with 10% $NaHCO_3$. A crude reaction product was purified by silica gel column eluting with hexane-ethylacetate to give 2-ethylhexyl-*trans*-substituted cinnamate.

2-ethylhexyl-2-hydroxycinnamate (**1E**): yellow oil (45% yield) ^{1}H-NMR ($CDCl_3$) δ(ppm): 8.11-8.07 (d, J = 16.0 Hz, 1H), 7.45-7.44 (d, J=8 Hz, 1H), 7.23-7.20 (t, 1H), 6.92-6.90 (d, J=8 Hz, 1H), 6.89-6.85 (t, 1H), 6.70-6.65 (d, J = 16.0 Hz, 1H); ^{13}C-NMR ($CDCl_3$) δ(ppm): 169.2, 155.9, 141.2, 131.5, 129.2, 121.7, 120.4, 118.4, 116.5, 67.3, 38.9, 30.3, 29.3, 24.0, 23.1, 14.1, 11.0.

2-ethylhexyl-3-hydroxycinnamate (**2E**): yellow oil (65% yield) ^{1}H-NMR ($CDCl_3$) δ(ppm): 7.62-7.58 (d, J = 16.0 Hz, 1H), 7.25- 7.21 (dd, 1H), 7.08-7.06 (d, J=8Hz, 1H), 7.00 (s, 1H) 6.87-6.85 (d, J=8 Hz, 1H), 6.41-6.37 (d, J = 16.0 Hz, 1H), 1.64-0.86 (m, 15H); ^{13}C-NMR ($CDCl_3$) δ(ppm): 169.2, 156.6, 145.4, 135.6, 129.9, 120.5, 118.0, 117.8, 114.7, 65.1, 30.3, 28.9, 26.2, 25.1, 23.5, 14.0, 10.9.

2-ethylhexyl-4-hydroxycinnamate (**3E**): pale yellow oil (60% yield) ^{1}H-NMR ($CDCl_3$) δ(ppm): 7.56-7.52 (d, J = 16.0 Hz, 1H), 7.33-7.31 (d, J=8 Hz, 2H), 6.80-6.78 (d, J=8 Hz, 2H), 6.23-6.19 (d, J = 16.0 Hz, 1H), 4.05-4.03 (dd, 2H), 1.59-0.79 (m, 15H); ^{13}C-NMR ($CDCl_3$) δ(ppm): 168.2, 158.2, 144.7, 130.0, 126.8, 115.9, 115.2, 67.1, 38.8, 30.4, 28.9, 23.8, 22.9, 14.0, 11.0.

2-ethylhexyl-2-nitrocinnamate (**4E**): yellow oil (55% yield) ^{1}H-NMR ($CDCl_3$) δ(ppm): 7.56-7.52 (d, J = 16.0 Hz, 1H), 7.29-7.25 (dd, J = 7.79 Hz, 1H), 7.19-7.15 (t, 1H)), 7.12 (d, J = 9 Hz, 1H), 7.01-6.96 (t, 1H), 6.37-6.33 (d, J = 16.0 Hz, 1H), 4.06-4.03 (dd, 2H), 1.58-0.80 (m, 15H); ^{13}C-NMR ($CDCl_3$) δ(ppm): 165.9, 139.7, 133.4, 130.5, 130.2, 129.0, 124.8, 123.3, 67.3, 38.7, 30.4, 28.8, 23.8, 22.9, 23.9, 10.9.

2-ethylhexyl-3-nitrocinnamate (**5E**): yellow oil (60% yield) ^{1}H-NMR ($CDCl_3$) δ(ppm): 8.37 (s, 1H), 8.22-8.20 (d, J = 8 Hz, 1H), 7.82-7.80 (d, J = 8 Hz, 1H), 7.70-7.66 (d, J = 16.0 Hz, 1H), 7.58-7.54 (t, 1H), 6.57-6.53 (d, J = 16.0 Hz, 1H), 4.14-4.12 (d, J = 8 Hz, 2H), 1.65-0.87 (m, 15H); ^{13}C-NMR ($CDCl_3$) δ(ppm): 166.3, 148.7, 141.6, 136.3, 133.7, 128.9, 124.5, 122.4, 121.6, 67.3, 38.6, 30.1, 29.1, 23.9, 22.9, 14.0, 10.9.

2-ethylhexyl-4-nitroxycinnamate (**6E**): yellow oil (56% yield) ^{1}H-NMR ($CDCl_3$) δ(ppm): 8.17-8.15 (d, J = 8 Hz, 1H), 7.64-7.60 (d, J = 16.0 Hz, 1H), 7.61-7.59 (d, J=8 Hz, 1H), 6.51-6.47 (d, J = 16.0 Hz, 1H), 4.08-4.06 (dd, 2H), 1.61- 0.81 (m, 15H); ^{13}C-NMR ($CDCl_3$) δ(ppm): 171.6, 141.4, 128.6, 123.8, 122.6, 69.1, 38.7, 30.2, 28.8, 23.7, 22.8, 13.9, 10.8.

2-ethylhexyl-2-fluorocinnamate (**7E**): yellow oil (60% yield) ^{1}H-NMR ($CDCl_3$) δ(ppm): 7.80-7.76 (d, J = 16.0 Hz, 1H), 7.54-7.50 (t, 1H), 7.35-7.30 (dd, 1H), 7.15-7.12 (t, 1H), 7.10-7.05 (dd, 1H), 6.54-6.50 (d, J = 16.0 Hz, 1H), 4.18-4.16 (d, J = 8 Hz, 2H), 1.67-0.86 (m, 15H); ^{13}C-NMR ($CDCl_3$) δ(ppm): 167.0, 162.6, 137.1, 131.6, 129.1, 124.4, 120.9, 116.3, 116.1, 67.1, 38.7, 29.7, 29.0, 23.9, 22.7, 14.1, 11.0.

2-ethylhexyl-3-fluorocinnamate (**8E**): yellow oil (57% yield) ^{1}H-NMR ($CDCl_3$) δ(ppm): 7.80-7.76 (d, J = 16.0 Hz, 1H), 7.54- 7.50 (t, 1H), 7.35-7.30 (dd, 1H), 7.15-7.12 (t, 1H), 7.10-7.05 (dd, 1H), 6.54-6.50 (d, J = 16.0 Hz, 1H), 4.18-4.17 (d, 2H), 1.69-0.86 (m, 15H); ^{13}C-NMR ($CDCl_3$) δ(ppm): 166.6, 142.9, 136.7, 130.3, 123.9, 119.6, 117.0, 116.8, 114.3, 67.0, 38.8, 30.4, 28.8, 23.7, 22.9, 13.9, 10.9.

2-ethylhexyl-4-fluorocinnamate (**9E**): yellow oil (51% yield) ^{1}H-NMR ($CDCl_3$) δ(ppm): 7.63-7.59 (d, J = 16.0 Hz, 1H), 7.51-7.47 (dd, 2H), 7.07-7.03 (dd, 1H), 6.36-6.32 (d, J = 16.0 Hz, 11H), 4.18-4.16 (d, 2H), 1.58-0.86 (m, 15H); ^{13}C-NMR ($CDCl_3$) δ(ppm): 167.0, 143.1, 129.8, 118.0, 115.7, 67.0, 61.9, 38.8, 30.4, 28.9, 23.8, 13.9, 10.9.

Photostability: The photostability of each compound was tested in methanol solution. The fresh sample solution was irradiated with a broadband UVB lamp (Daavlin, OH) at room temperature. UV intensity was measured by using a UVB power meter (Optix Tech, Ltd., DC). UV absorption profiles of the irradiated samples were analyzed on a UV−Vis spectrometer (PerkinElmer, CT, USA). The photostability of each compound was examined by the relative absorbance at the maximum absorption wavelength of the compound. All experiments were done in triplicate. The photostability (S) was evaluated as:

$$S = I_{\mathrm{irr}} / I_{\mathrm{unirr}}$$

where I_{irr} and I_{unirr} denote absorbance of irradiated and unirradiated samples, respectively. The photostability was examined after 5, 10, and 30 min of irradiation.

Table S1. Excitation Energies (E_{ex}), Absorption Wavelengths (λ_{abs}), Oscillator Strengths (f) and Dipole Moments (μ) in the Gas Phase and in Methanol Solution for Nine Substituted Cinnamic Acids (**1A–9A**) Calculated Using the Direct SAC-CI Method.

	SAC-CI/D95(d)								Exp.
	State	E_{ex} (eV)	λ_{abs} (nm)	f	Excitation character	μ (D)[a]	$E_{ex(solv)}$[b]	$f_{(solv)}$[b]	(nm)
1A	XA'					(3.54)			
	$1A'$	3.88	320	0.281	H→L (38%), H-1→L (16%)	4.37	3.69	0.210	324
	$2A'$	4.51	275	0.236	H-1→L (36%), H→L (21%)	3.71	4.37	0.210	278
	$1A''$	4.82	257	0.000	H-3→L (31%), H-3→L+8 (13%)	0.11	5.03	0.000	
2A	XA'					(3.65)			
	$1A'$	4.01	309	0.084	H→L (29%), H-1→L (21%)	2.35	3.87	0.006	317
	$2A'$	4.52	274	0.426	H→L (31%), H-1→L (29%)	4.99	4.40	0.393	283
	$1A''$	4.82	257	0.000	H-3→L (36%), H-3→L+8 (14%)	0.11	5.00	0.000	
3A	XA'					(2.93)			
	$1A'$	4.16	298	0.335	H→L (36%), H→L+1 (22%)	4.61	3.96	0.212	300
	$2A'$	4.38	283	0.344	H→L+1 (27%), H→L (25%)	4.55	4.37	0.363	
	$1A''$	4.87	255	0.000	H-3→L (36%), H-3→L+11 (14%)	0.11	5.07	0.000	
4A	XA'					(5.79)			
	$1A'$	4.06	305	0.154	H→L (33%), H-1→L (15%)	3.16	3.81	0.128	
	$1A''$	4.39	282	0.000	H-4→L (31%), H-4→L+1 (18%)	0.08	4.58	0.000	
	$2A'$	4.64	267	0.351	H-1→L (26%), H→L (24%)	4.46	4.45	0.327	273
5A	XA'					(4.90)			
	$1A'$	4.15	299	0.079	H→L (30%), H-1→L (16%)	2.25	3.94	0.105	
	$1A''$	4.52	274	0.000	H-4→L+1 (27%), H-4→L (25%)	0.08	4.71	0.000	
	$2A'$	4.60	270	0.249	H→L+1 (27%), H-1→L (26%)	3.78	4.47	0.219	274
6A	XA'					(3.43)			
	$1A'$	4.12	301	0.033	H-1→L (36%), H→L+2 (17%)	1.45	3.95	0.000	
	$2A'$	4.33	286	0.767	H→L (61%), H-1→L (10%)	6.83	3.92	0.021	
	$1A''$	4.35	285	0.000	H-4→L (31%), H-4→L+1 (19%)	0.09	4.09	0.685	282
7A	XA'					(3.29)			
	$1A'$	4.23	293	0.244	H→L (31%), H-1→L (24%)	3.90	4.11	0.097	
	$1A''$	4.51	275	0.000	H-3→L (43%), H-3→L+2 (24%)	0.09	4.69	0.000	
	$2A'$	4.53	274	0.266	H-1→L (28%), H→L (26%)	3.93	4.44	0.308	265
8A	XA'					(2.44)			
	$1A'$	4.32	287	0.043	H-1→L (34%), H→L+1 (24%)	1.62	4.27	0.084	
	$1A''$	4.53	274	0.000	H-3→L (46%), H-3→L+2 (25%)	0.09	4.70	0.000	
	$2A'$	4.56	272	0.552	H→L (48%), H→L+1 (13%)	5.65	4.44	0.388	266
9A	XA'					(1.28)			
	$1A'$	4.38	283	0.238	H→L (29%), H→L+1 (25%)	3.78	4.37	0.252	
	$1A''$	4.56	272	0.000	H-3→L (44%), H-3→L+2 (23%)	0.09	4.74	0.000	
	$2A'$	4.58	271	0.406	H→L (32%), H→L+1 (22%)	4.83	4.45	0.287	269

[a] Values in parentheses show the dipole moment of the ground state (XA').

[b] Solvent effect is calculated by PCM-TD-CAM-B3LYP in methanol solution from Ref. 27.

Table S2. Excitation Energies (E_{ex}), Emission Wavelengths (λ_{em}), Oscillator Strengths (f), Radiative Lifetimes (τ) and Dipole Moments (μ) for Nine Substituted Cinnamic Acids (**1A–9A**) Calculated Using the Direct SAC-CI Method.

	SAC-CI/D95(d)						
	State	E_{ex} (eV)	λ_{em} (nm)	f	τ (ns)	Transition character	μ (D)[a]
1A	1A'	3.51	353	0.437	4.28	H→L (50%)	5.73 (4.63)
2A	1A'	3.68	337	0.255	6.69	H→L (46%)	4.27 (4.19)
3A	1A'	3.62	343	0.597	2.95	H→L (67%)	6.60 (3.88)
4A	1A'	3.76	330	0.377	4.33	H→L (48%)	5.14 (7.99)
5A	1A'	3.74	332	0.255	6.49	H→L (44%)	4.24 (5.29)
6A	1A'	4.00	310	0.840	1.72	H→L (76%)	7.45 (5.60)
7A	1A'	3.76	330	0.525	3.11	H→L (48%)	6.07 (4.26)
8A	1A'	3.96	313	0.472	3.12	H→L (50%)	5.61 (2.84)
9A	1A'	3.83	323	0.570	2.75	H→L (58%)	6.26 (1.66)

[a] Values in parentheses show the dipole moment of the ground state (XA').

Table S3. Absorption wavelengths (nanometers) in gas phase and in methanol solution for nine various substituted methyl cinnamates (**1E-9E**) using TD-B3LYP, TD-CAM-B3LYP, SAC-CI compared with the experimental values.

	Gas phase						In methanol						*Exp.*
	B3LYP*		CAM-B3LYP*		SAC-CI		B3LYP*		CAM-B3LYP*		SAC-CI		MeOH
	λ_{abs}	|Error|	λ_{abs}	|Error|	λ_{abs}	|Error|	λ_{abs}	|Error|	λ_{abs}	|Error|	λ_{abs}	|Error|	
1E	312	20	288	44	323	9	332	0	302	30	341	9	332
	273	7	253	27	275	5	285	5	261	19	285	5	280
2E	313	12	278	47	310	15	331	6	289	36	323	2	325
	273	12	258	27	273	12	284	1	265	20	281	4	285
3E	295	19	277	37	299	15	313	1	291	23	315	1	314
4E	261	20	296	15	268	13	271	10	315	34	279	2	281
5E	261	21	281	1	269	13	277	5	294	12	277	5	282
6E	315	11	285	19	282	22	339	35	301	3	298	6	304
7E	287	1	269	19	272	16	296	8	277	11	279	9	288
8E	271	13	265	19	269	15	279	5	273	11	278	6	284
9E	282	3	266	13	269	10	292	13	275	4	278	1	279

*Absorption wavelength is calculated by TD-B3LYP and TD-CAM-B3LYP in gas phase and methanol solution from Ref. 27

Table S4. Absorption wavelengths (nanometers) in gas phase and in methanol solution for nine various substituted cinnamic acids (**1A-9A**) using TD-B3LYP, TD-CAM-B3LYP, SAC-CI compared with the experimental values.

	Gas phase						In methanol						*Exp.*
	B3LYP*		CAM-B3LYP*		SAC-CI		B3LYP*		CAM-B3LYP*		SAC-CI		MeOH
	λ_{abs}	|Error|	λ_{abs}	|Error|	λ_{abs}	|Error|	λ_{abs}	|Error|	λ_{abs}	|Error|	λ_{abs}	|Error|	
1A	313	11	288	36	320	4	332	8	302	22	336	12	324
	273	5	254	24	275	3	285	7	261	17	284	6	278
2A	317	0	280	37	309	8	331	14	289	28	320	3	317
	273	10	258	25	274	9	283	0	265	18	282	1	283
3A	295	5	277	23	298	2	312	12	290	10	313	13	300
4A	260	13	295	22	267	6	270	3	314	41	279	6	273
5A	260	14	280	6	270	4	276	2	293	19	277	3	274
6A	313	31	283	1	286	4	337	55	300	18	303	21	282
7A	288	23	270	5	274	9	296	31	277	12	279	14	265
8A	272	6	265	1	272	6	278	12	272	6	279	13	266
9A	282	13	267	2	271	2	291	22	275	6	279	10	269

*Absorption wavelength is calculated by TD-B3LYP and TD-CAM-B3LYP in gas phase and methanol solution from Ref. 27

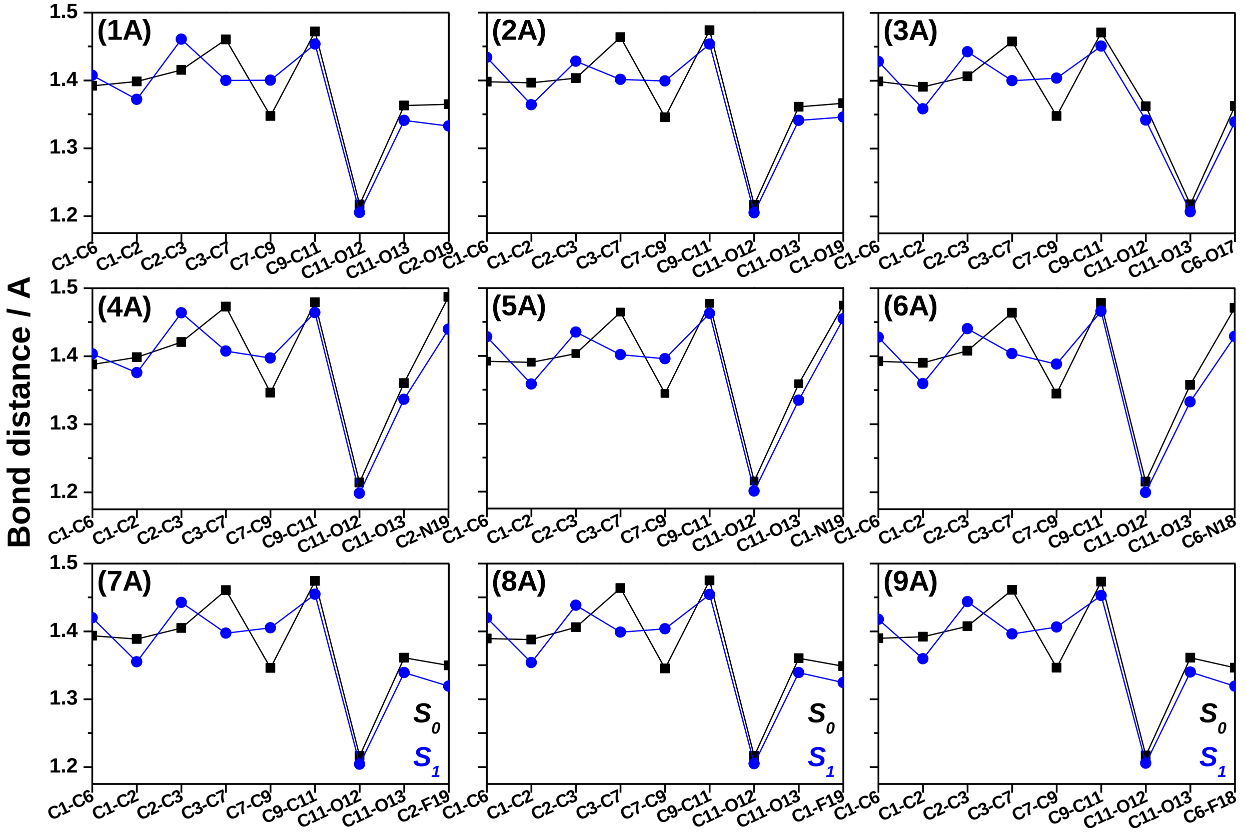


Figure S1. Bond lengths of nine substituted cinnamaic acids (**1A–9A**) in the S_0 and S_1 states calculated using the B3LYP/6-31G(d) and CIS/D95(d) methods, respectively.

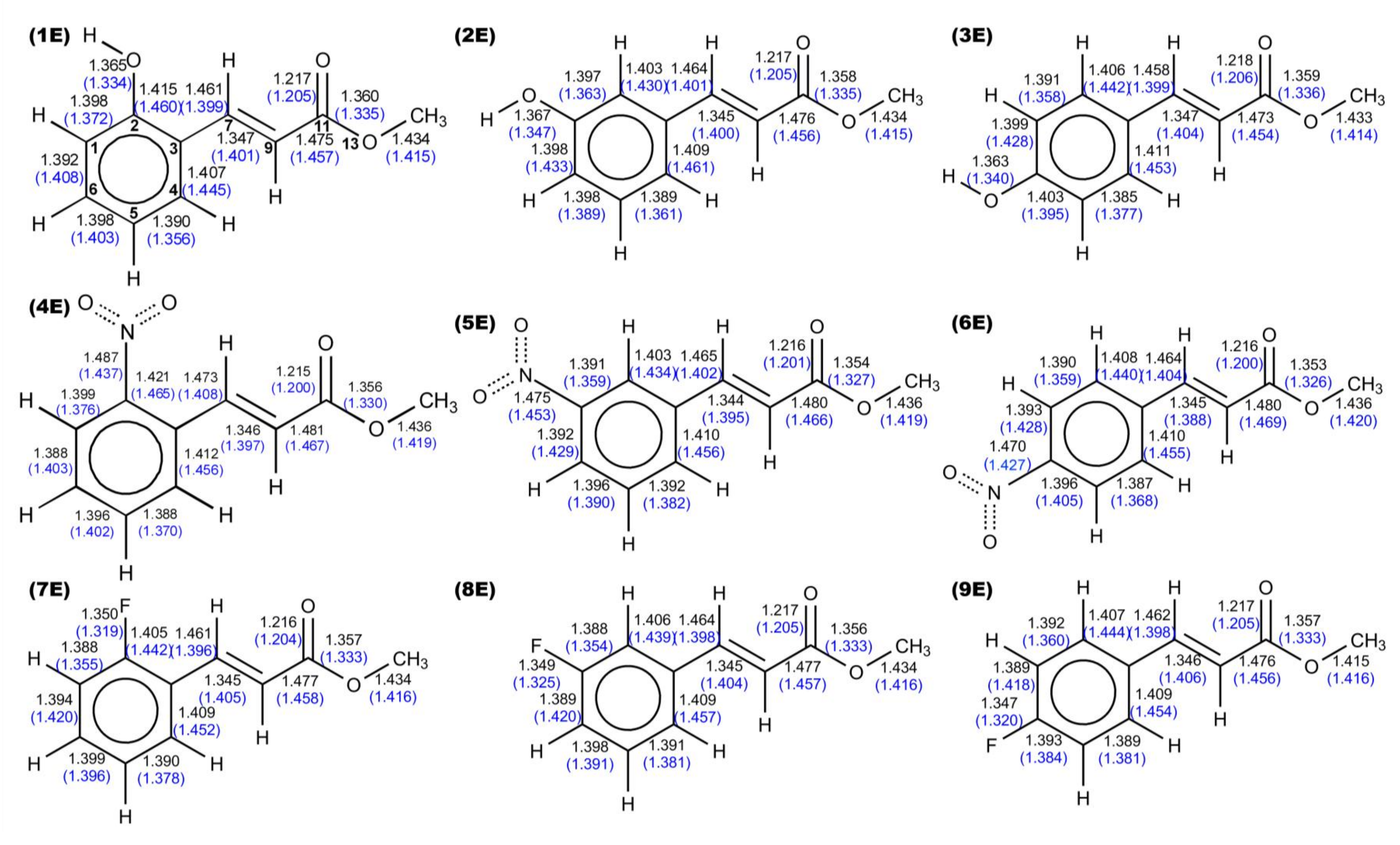


Figure S2. A comparison of the bond lengths (in Å) between the S_0 and S_1 (in parentheses) states for nine substituted methyl cinnamates (**1E–9E**) calculated using the B3LYP/6-31G(d) and CIS/D95(d) methods, respectively.

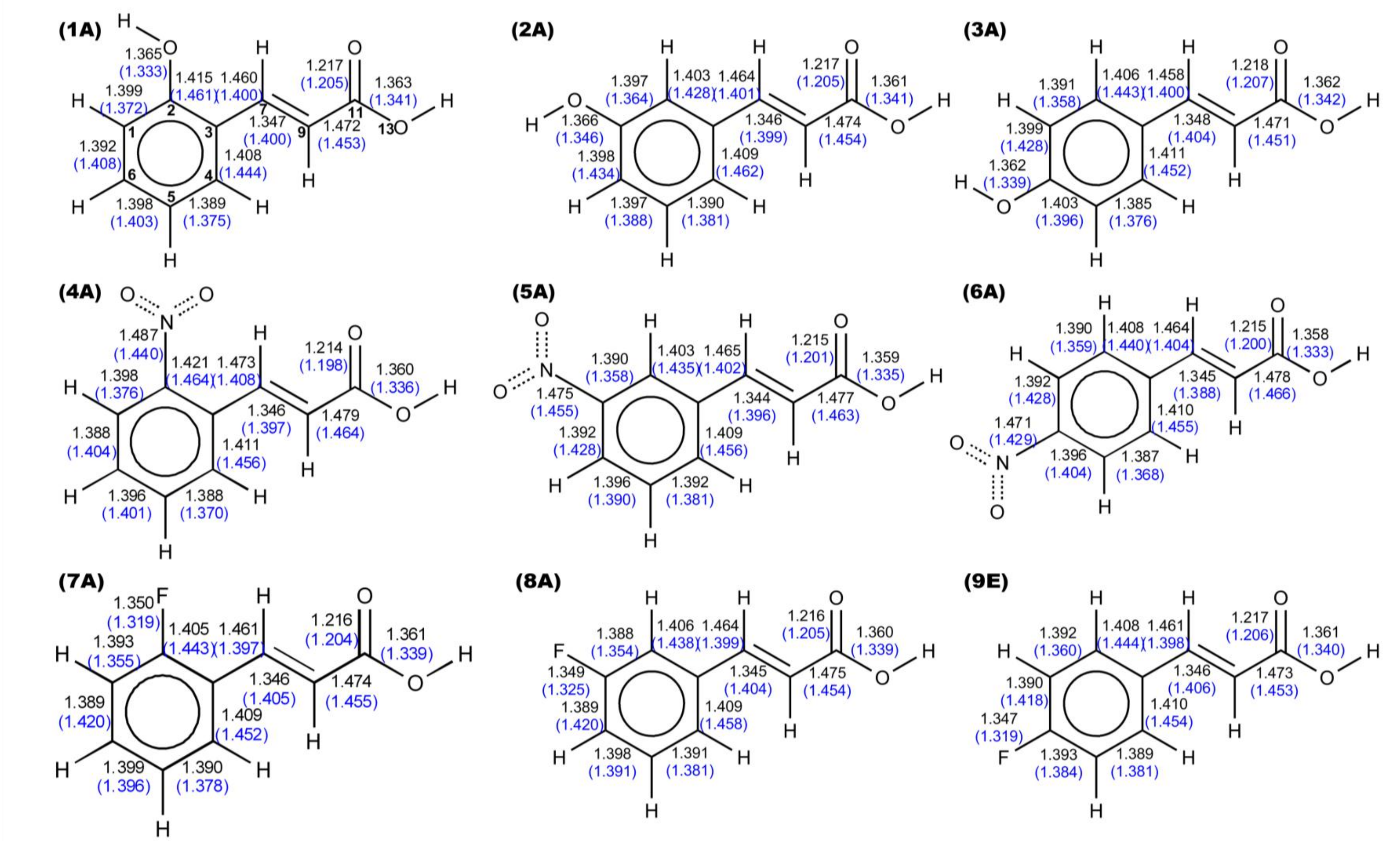


Figure S3. A comparison of the bond lengths (in Å) between the S_0 and S_1 (in parentheses) states for nine substituted cinnamic acids (**1A–9A**) calculated using the B3LYP/6-31G(d) and CIS/D95(d) methods, respectively.

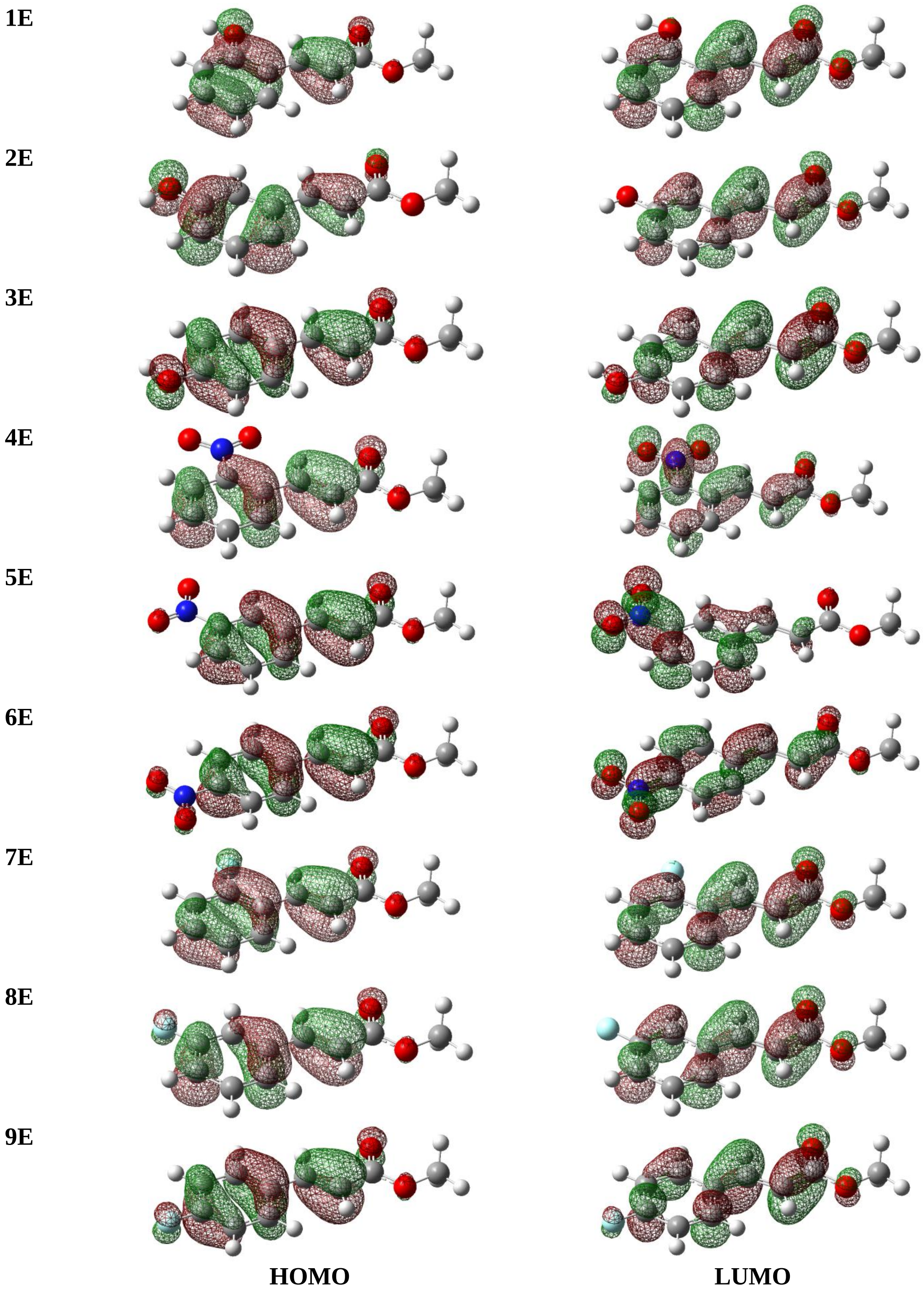


Figure S4. HOMO and LUMO of nine substituted methyl cinnamates (**1E**–**9E**).

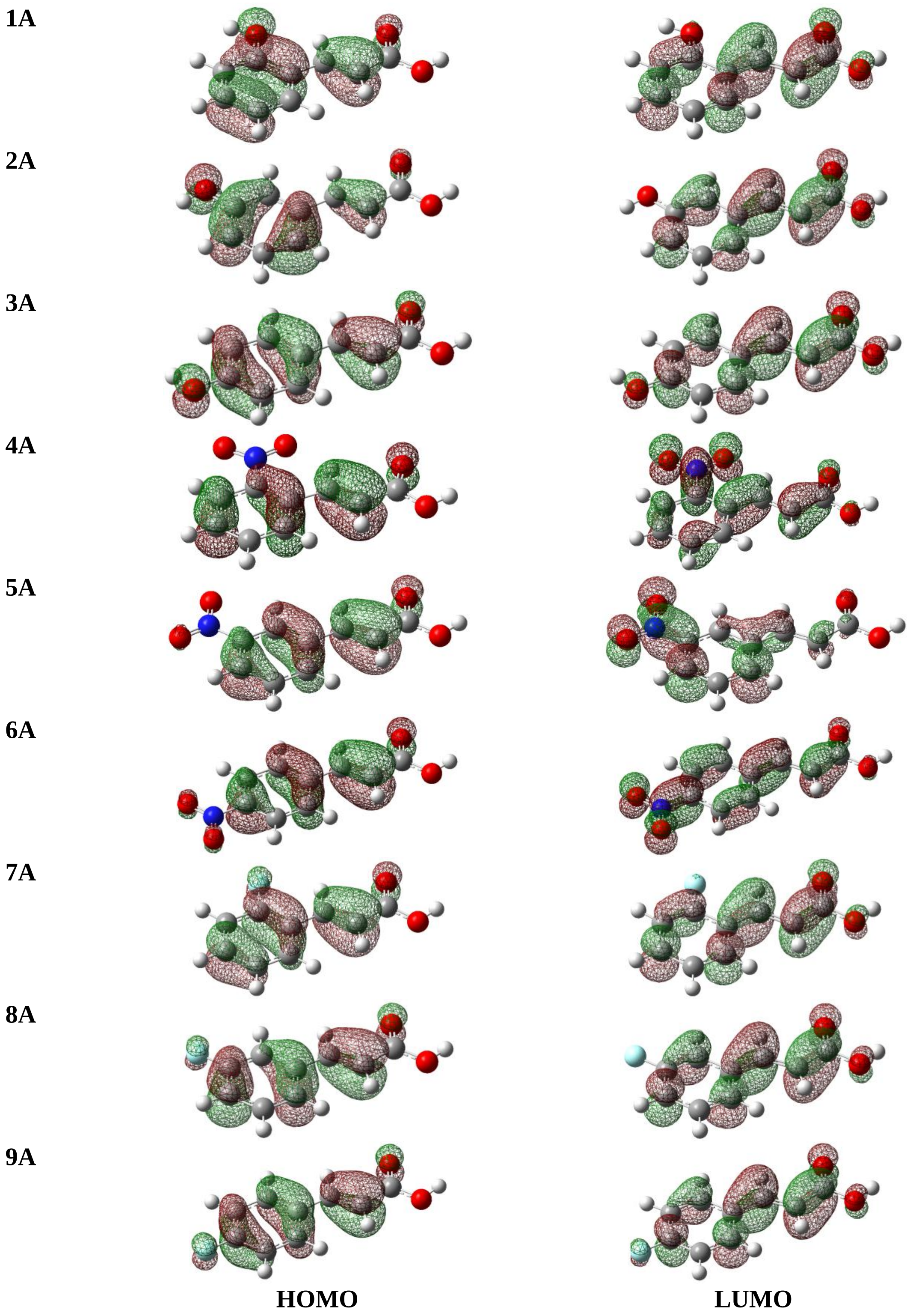


Figure S5. HOMO and LUMO of nine substituted cinnamic acids (**1A–9A**).

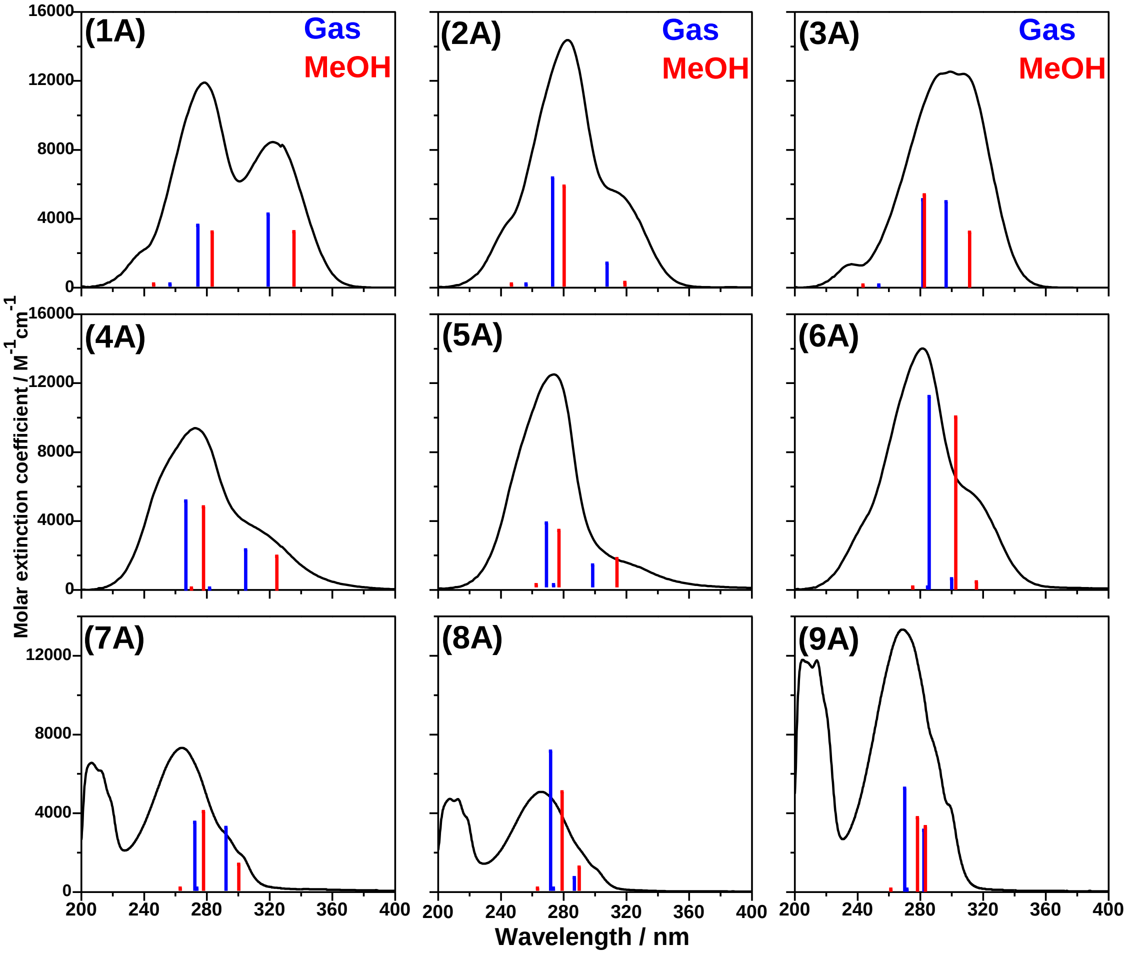


Figure S6. Absorption spectra of hydroxy (**1A–3A**), nitro (**4A–6A**), and fluoro (**7A–9A**) cinnamic acids substituted at the *ortho*, *meta*, and *para* positions calculated using the direct SAC-CI method in the gas phase (blue) and in methanol solution (red) compared with the experimental spectra.

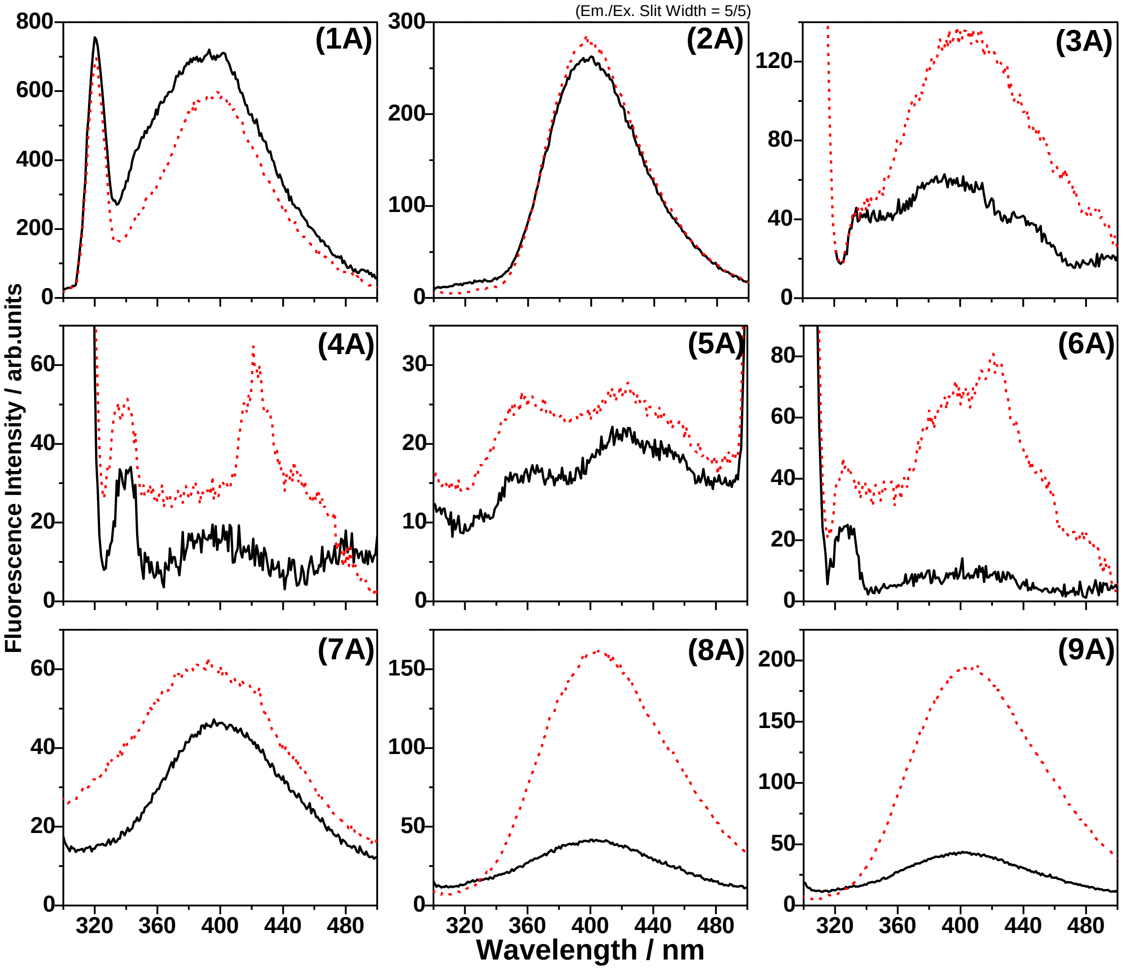


Figure S7. Emission spectra of hydroxy (**1A–3A**), nitro (**4A–6A**), and fluoro (**7A–9A**) cinnamic acids substituted at the *ortho*, *meta*, and *para* positions in the presence of oxygen (black line) and under nitrogen (red line).

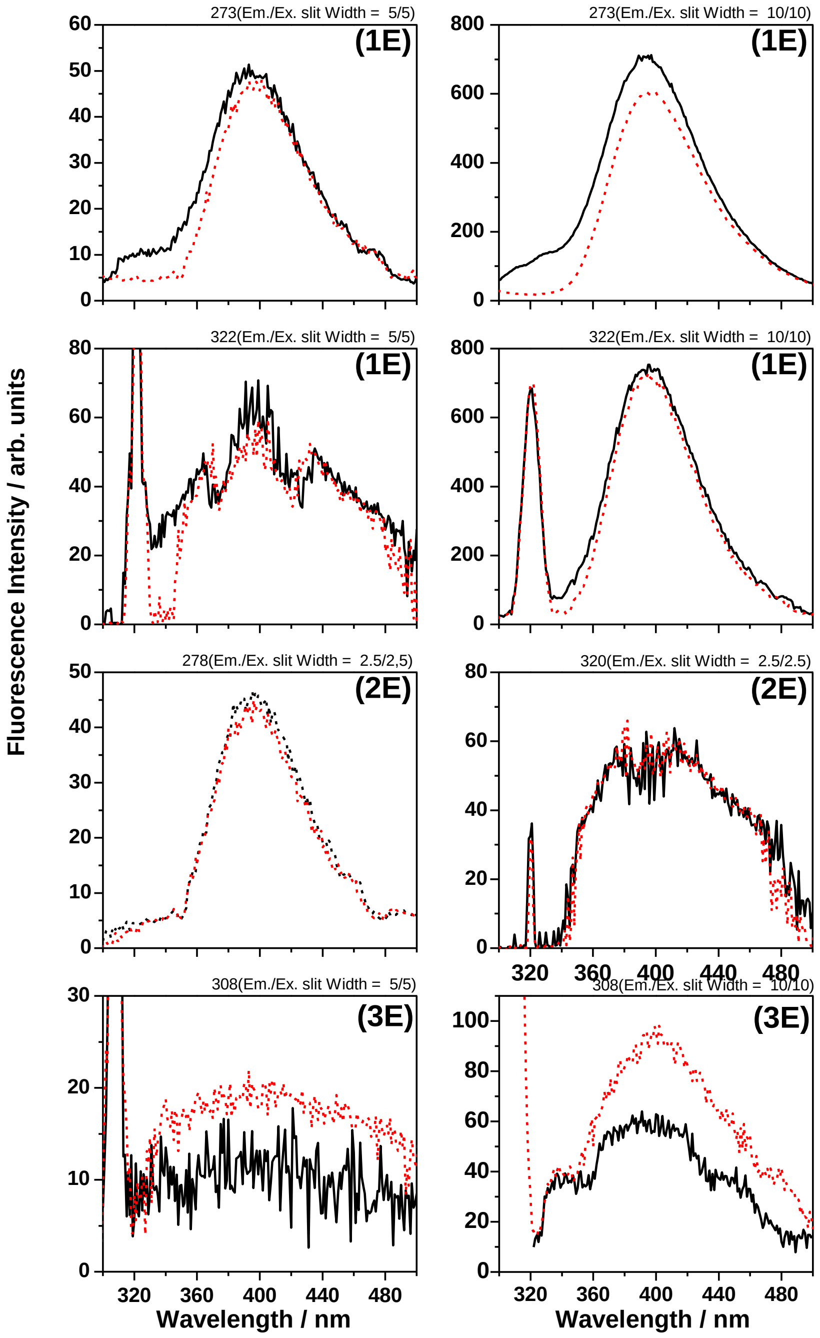


Figure S8. Emission spectra of hydroxy (**1E–3E**) cinnamates substituted at the *ortho*, *meta*, and *para* positions in the presence of oxygen (black line) and under nitrogen (red line). The excitation wavelength and emission/excitation slit width that affects the observed intensity are given in the top of each figure.

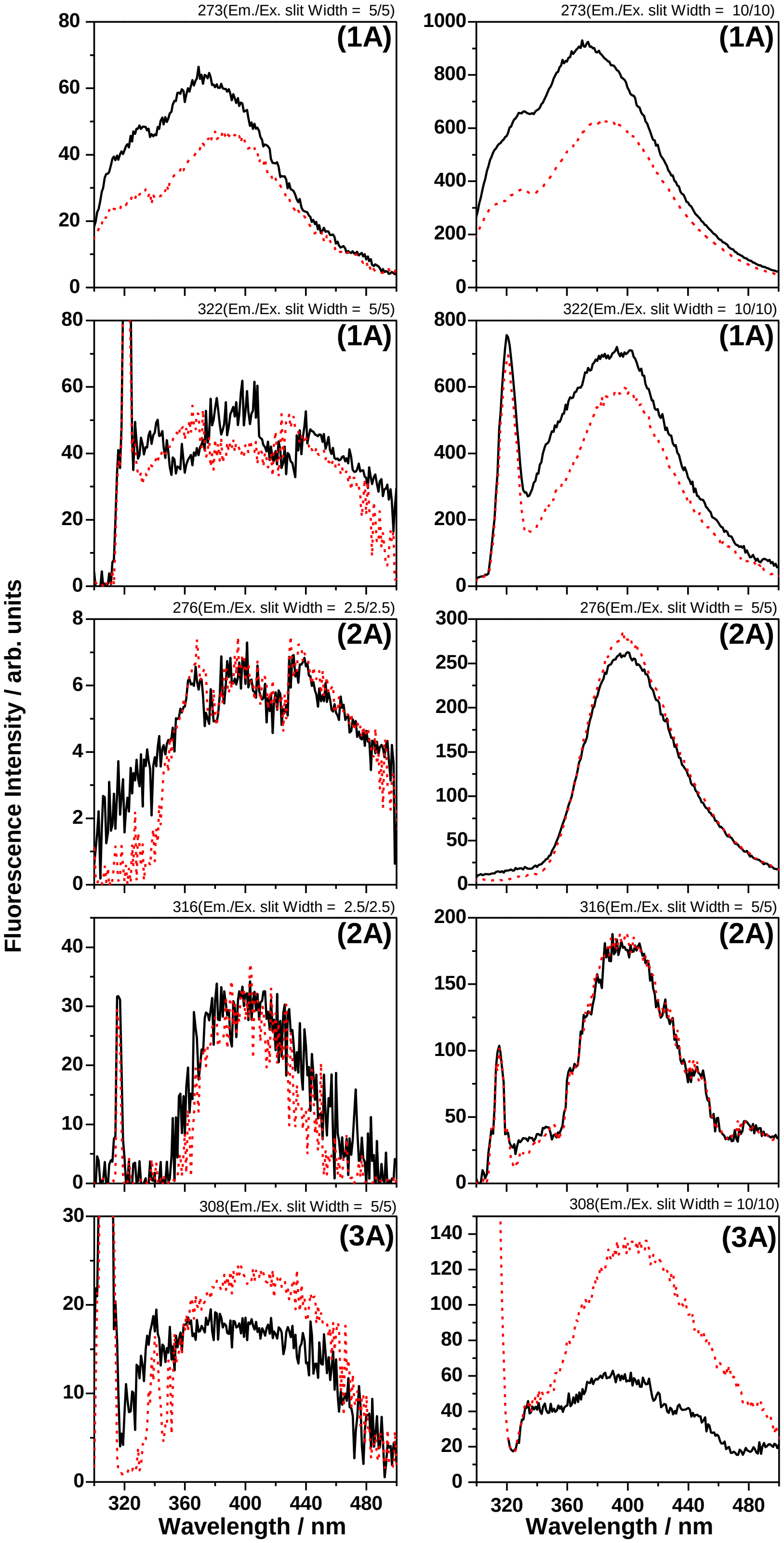


Figure S9. Emission spectra of hydroxy (**1A**–**3A**) cinnamic acids substituted at the *ortho*, *meta*, and *para* positions in the presence of oxygen (black line) and under nitrogen (red line). The excitation wavelength and emission/excitation slit width that affects the observed intensity are given in the top of each figure.

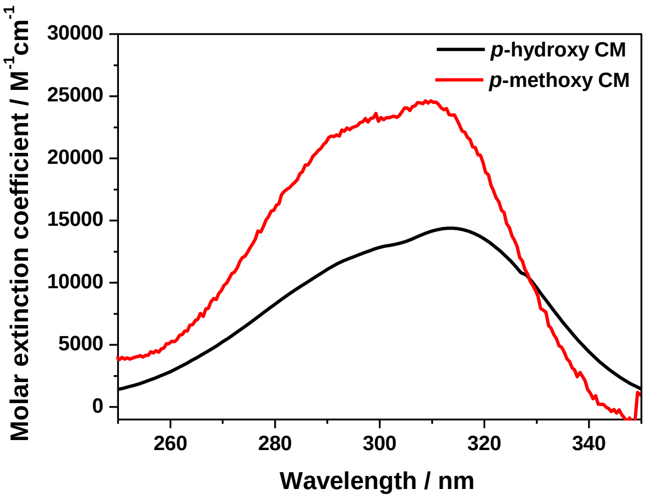


Figure S10. A comparison of the experimental absorption spectra in methanol between *para*-hydroxy-(**3E**) and *para*-methoxy cinnamates (Refs. 9 and 25).

Potential energy curves (PECs): The angle of the nitro group relative to the cinnamate unit θ ($C_1{=}C_2{-}N_{19}{=}O_{21}$) affects the optical properties as it relates to the π-conjugation. In particular, the *ortho*-nitro derivatives have non-planar structures in the S_0 state because of steric effects, as discussed later. Therefore, the ground state potential energy curves (S_0 PECs) along the angle θ of the nitro group with respect to the phenyl ring were calculated using the B3LYP/6-31G(d) method. Molecular structures were partially optimized at fixed angles (θ = 0° to 180° in steps of 15°) with all the other coordinates optimized. With these structures, the excitation energies were calculated to examine their dependence on the angle.

We discuss here the structure of nitro-substituted methyl cinnamates. The ground-state (S_0) PECs for the rotation of the nitro group relative to the plane of the phenyl ring were calculated using the B3LYP/6-31G(d) method. *Ortho*-(**4E**), *meta*-(**5E**), and *para*-(**6E**) nitro methyl cinnamates were examined for the angle θ ($C_1{=}C_2{-}N_{19}{=}O_{21}$). The S_0 PECs were partially optimized at fixed angles (θ = 0° to 180° in steps of 15°) with all the other coordinates optimized using the B3LYP/6-31G(d) method. The PECs of these derivatives are shown in Fig. S11.

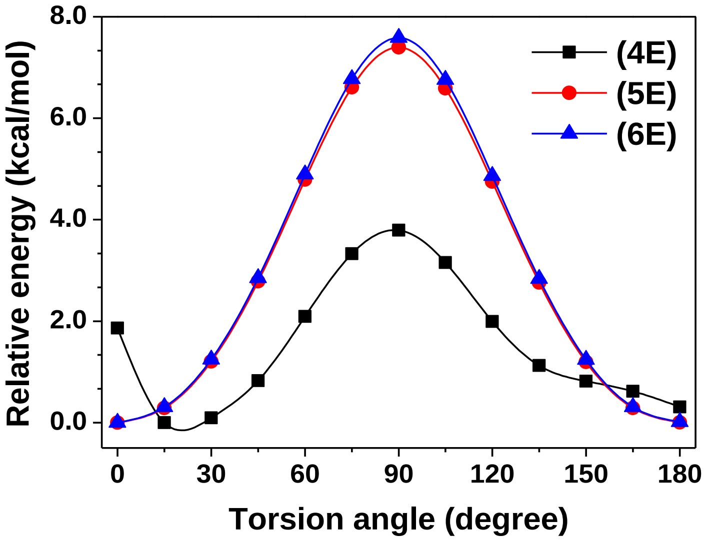


Figure S11. Ground-state PECs along the torsion angle ($C_1{=}C_2{-}N_{19}{=}O_{21}$) of NO_2 to the molecular plane for the nitrocinnamates (**4E–6E**) calculated using the B3LYP/6-31G(d) method.

The most stable conformation was located at $\theta = 0°$ for **5E** and **6E** and $\theta = \sim 15°$ for **4E**. At $\theta = 90°$, the calculated energy barriers relative to the most stable conformation for **4E**, **5E**, and **6E** were 3.79, 7.40, and 7.59 kcal/mol, respectively. Note that the propenyl unit is also not coplanar to the benzene unit in **4E**. The low rotational energy barrier of about 1.0 kcal/mol in the range of $\theta = 0°–30°$ for **5E** and **6E** and $\theta = 10°–45°$ for **4E** indicates that a certain range of non-planar conformations contributes to the absorption spectra at room temperature. Therefore, the SAC-CI absorption spectra of the nitro compounds in the non-planar structure were examined. The calculated spectra for $\theta = 0°$, 15°, and 30° of **4E**, **5E,** and **6E** are shown in Fig. S12. The trend of absorption peaks for these compounds along this angle does not change much. In the *ortho* derivative (**4E**), the peaks show blue shift at $\theta = 15°$ relative to the planar structure, while this shift is relaxed at $\theta = 30°$. The ratio of the peak intensity between the first and second ππ* transitions change with regard to the angle, which is related to the single absorption peak nature of **4E**. On the other hand, the peaks of the *meta*-(**5E**) and *para*-(**6E**) derivatives show small shifts.

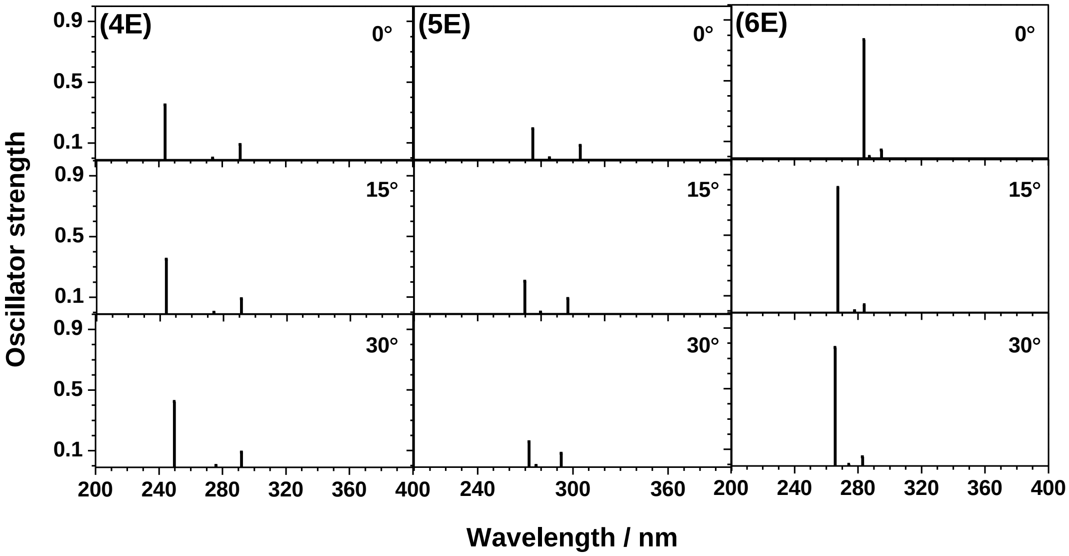


Figure S12. SAC-CI absorption spectra for the nitro methyl cinnamates **(4E–6E)** at angle ($C_1=C_2–N_{19}=O_{21}$) of $\theta = 0°$, 15° and 30° calculated using the SAC-CI/D95(d) method.

Stability and identification of its photo-degradation product

Following the degradation by HPLC: Analysis during the degradation product was done at 25°C using a CLIPEUS 18 column (partical size 5μm, 150x3.0 mm I.D.; Higgins Analytical, Inc). The mobile phase used was methanol:water (90/10 v/v) at a flow rate of 0.5 ml/min. The UV detector was set at the maximum absorption for each compound. The 1000 p.p.m. stock solution was diluted 100 times with pure methanol before injection. The sample injection volume was 10 μl. The sample solution was irradiated with a broadband UVB lamp (Daavlin, OH).

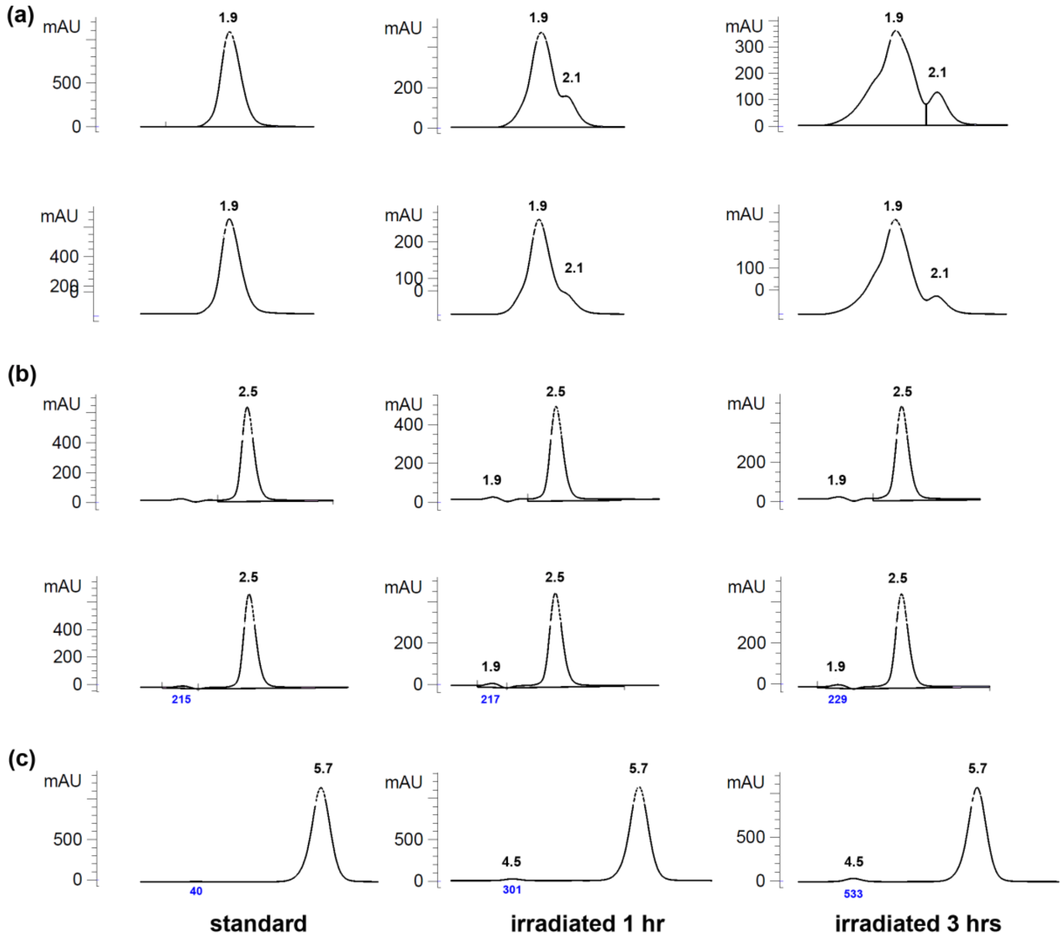
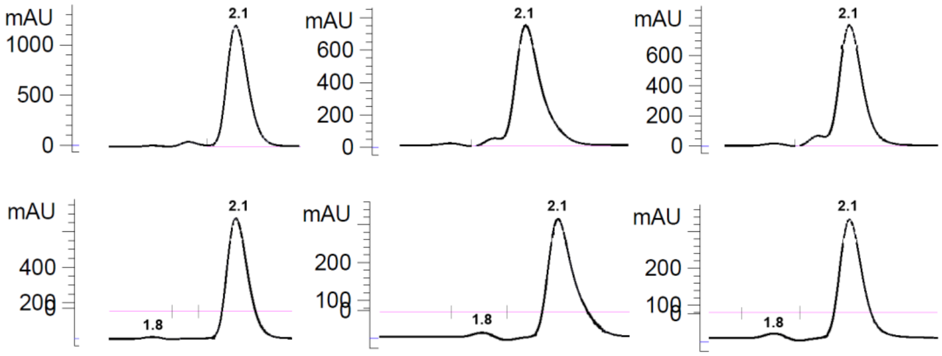


Figure S13. Chromatograms of (a) *ortho*-(**1E**) (b) *meta*-(**2E**) and (c) *para*-(**3E**)-hydroxy cinnamate before and after light irradiated at1 hr and 3 hrs. The HPLC was done at 25°C using a CLIPEUS 18 column. The mobile phase used was methanol:water (90:10 v/v) at the flow rate of 0.5 mL min^{-1}. The UV detector was set at 280 (above) and 332 (below) nm for **1E**, 285 (above) and 325 (below) nm for **2E** and 314 nm for **3E**. The sample injection volume was 10 μL. Peak area of side product is shown in blue color.

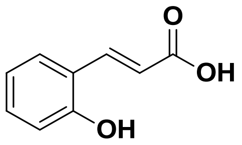
*Ortho-hydroxycinnamic acid (***1A***) and its photo-degradation product using HPLC-MS and NMR*: Collection of standard *ortho*-hydroxy cinnamic acid (**1A**) and its degradation product was done at 25°C using a CLIPEUS 18 column (partical size 5μm, 150x3.0 mm I.D.; Higgins Analytical, Inc). The mobile phase used was methanol:water (90/10 v/v) with trifluoroacetic acid (TFA) (0.01 v/v) at a flow rate of 0.2 ml/min. The UV detector was set at the 278 and 324 nm. The 1000 p.p.m. stock solution was diluted 100 times with pure methanol before injection. The sample injection volume was 10 μl for each compound. Positive-ion mass spectra were recorded corresponding to the each peak form HPLC chromatogram.

HPLC-MS and NMR of the light-exposed cinnamic acid (**1A**) indicated the presence of only the *trans*- and *cis*-cinnamic acid as given in Figures S14, S15 and S16. Although it has been known the possibility of *trans*-*ortho*-hydroxycinnamic acid are transformed to their *cis*-iomers on irradiation of UV light and might cyclize to give coumarin.[46] As the results, figure S14 show the HPLC chromatograms of **1A** as the UV detector at 324 nm revealed a new peak at retention time 1.9 min and therefore indicated an accumulation of a new product. Moreover, mass spectra of decomposed product are showed in Figure S15. Both spectra gave a protonated molecular peak at m/z of 147.3 and 103.4. The similarity between the two mass spectra confirmed that both compounds were isomerization. It should be mentioned here that all other peaks in the spectra correspond to the cluster ions of the mobile phase. NMR data revealed a *trans*-isomer for the standard **1A** and *cis*-isomer at the same position for the isolated photo-degradation product. NMR spectra of light exposed **1A** indicated the presence of new signal of *cis*-isomer at 5.82 ppm after irradiated at 30 and 60 min as shown in Figure S16.



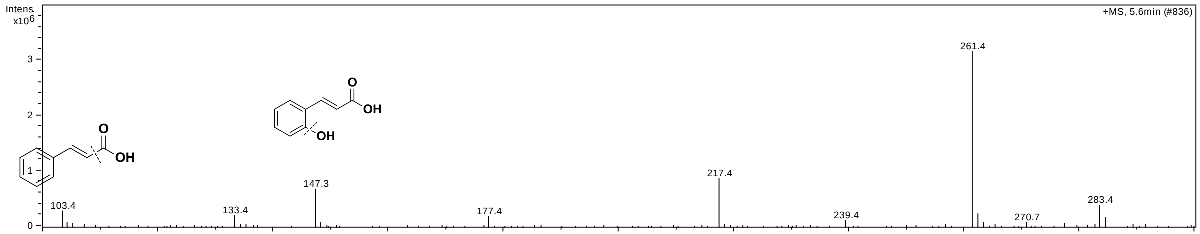
1A standard **irradiated 1 hr** **irradiated 3 hrs**

Figure S14. Chromatograms of standard *ortho*-hydroxycinnamic acid (**1A**) before and after light irradiated at1 hr and 3 hrs. The HPLC was done at 25°C using a CLIPEUS 18 column. The mobile phase used was methanol:water (90:10 v/v) at the flow rate of 0.5 mL min^{-1}. The UV detector was set at 278 (above) and 324 (below) nm. The sample injection volume was 10 μL.

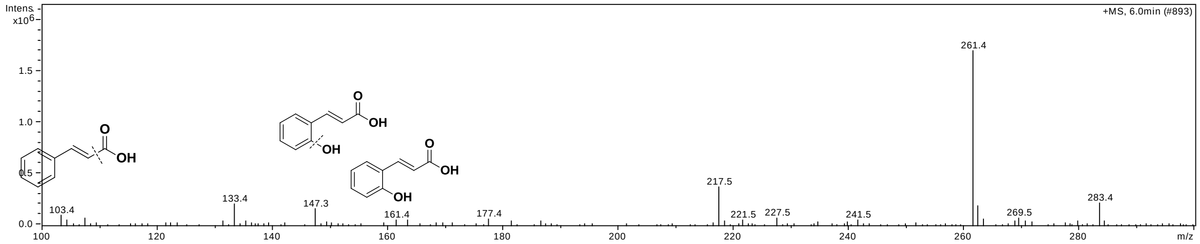


Chemical Formula: $C_9H_8O_3$
Exact Mass: 164.05
Molecular Weight: 164.16
m/z: 164.05 (100.0%), 165.05 (9.9%), 166.05 (1.0%)
Elemental Analysis: C, 65.85; H, 4.91; O, 29.24

At retention time of 4.6



At retention time of 5.4



Mobile Phase (Methanol:Water 90:10 v/v) + TFA 0.01 v/v

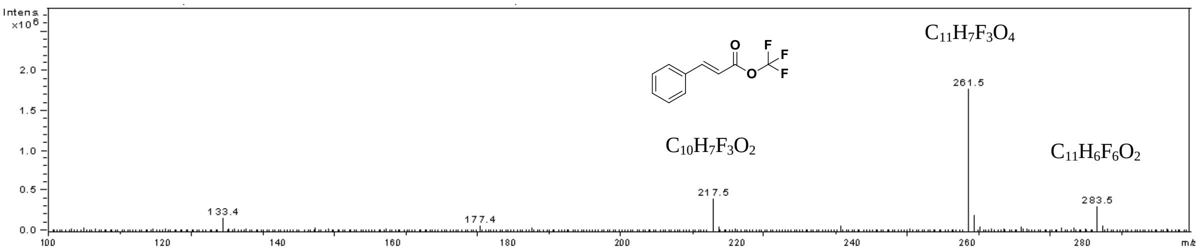


Figure S15. Mass spectra of the peaks from HPLC chromatogram for *ortho*-hydroxycinnamic acid (**1A**). The HPLC was done at 25°C using a CLIPEUS 18 column. The mobile phase used was methanol:water (90:10 v/v) with trifluoroacetic acid (TFA) 0.01 v/v at the flow rate of 0.2 mL min^{-1}. The sample injection volume was 10 μL.

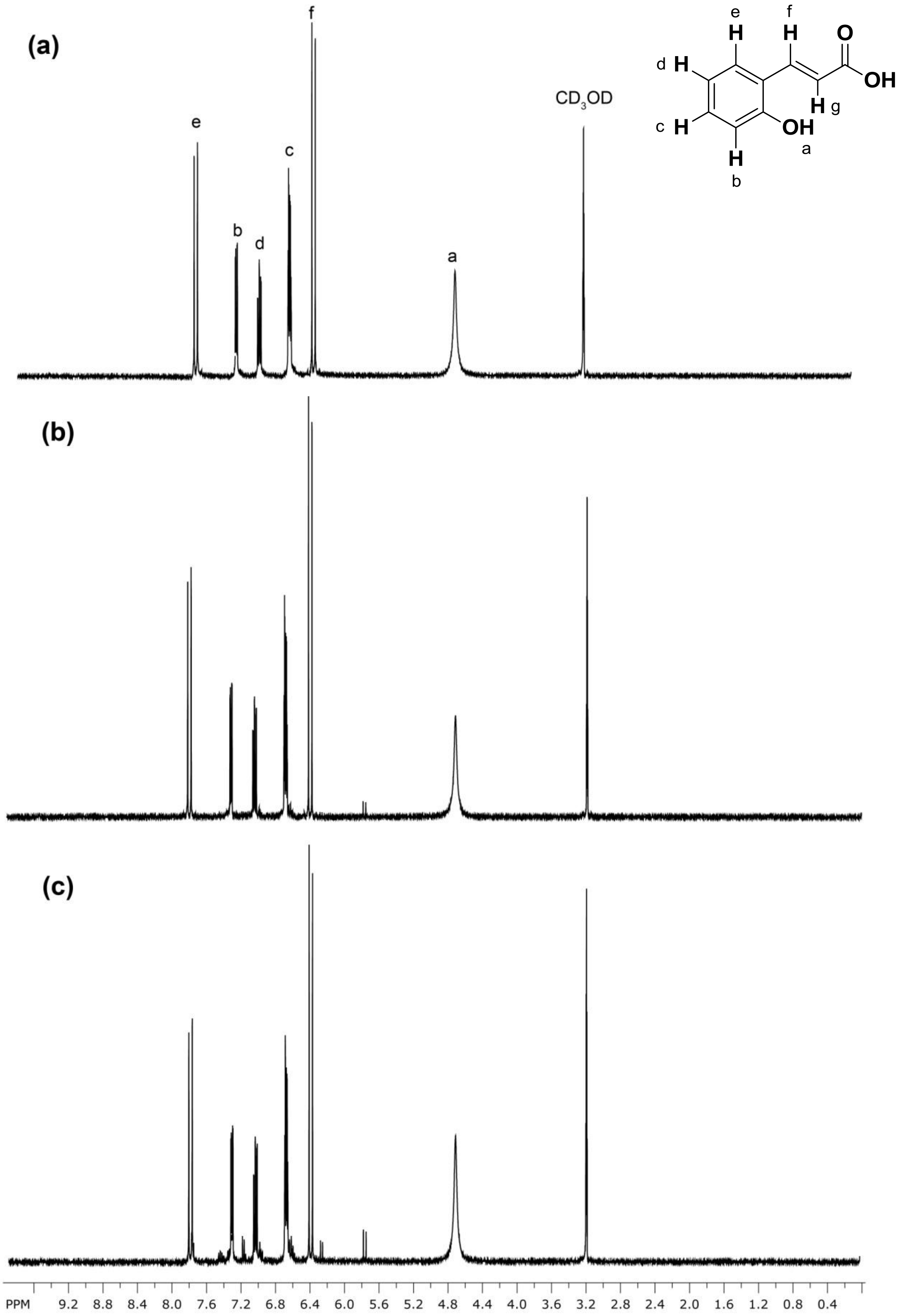


Figure S16. ^{1}H NMR (400 MHz) of *ortho*-hydroxy cinnamic acid **(1A)** (a) before, (b) after light irradiated at 30 min and (c) 120 min. (deuterated methanol as solvent).